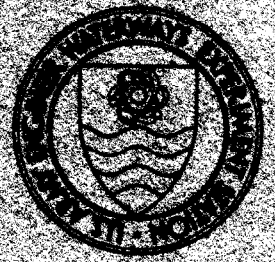




DREDGED MATERIAL RESEARCH PROGRAM



MISCELLANEOUS PAPER D-74-14

DISCUSSION OF REGULATORY CRITERIA FOR OCEAN DISPOSAL OF DREDGED MATERIALS: ELUTRIATE TEST RATIONALE AND IMPLEMENTATION GUIDELINES

by

J. W. Keeley, R. M. Engler



March 1974

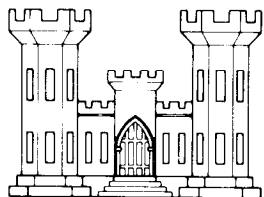
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Vicksburg, Mississippi

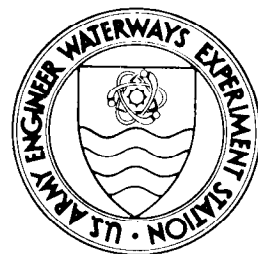
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FOREWORD

Under authority contained in Section 123(i) of Public Law 91-611, the Corps of Engineers is conducting a comprehensive research program concerning the disposal of dredged material. Actual program planning, management, and implementation have been delegated to the U. S. Army Engineer Waterways Experiment Station (WES) where the program, designated the Dredged Material Research Program (DMRP), is being administered by the Office of Dredged Material Research (ODMR).

While several research efforts under the DMRP are concerned with the polluttional properties of dredged material and with the effects of polluted material on water quality and aquatic organisms, the development of regulatory criteria per se is beyond the scope of the DMRP. However, with the enactment of legislation regulating the disposal of wastes and dredged material in the oceans (Public Law 92-532, Marine Protection, Research, and Sanctuaries Act of 1972), the Corps of Engineers was placed in the role of cooperating with the Environmental Protection Agency (EPA) in the development of guidelines for dredged material disposal. Because of the existence of the DMRP and the staff expertise assembled for its conduct, ODMR staff members played a key role in formulating the guidelines, particularly the analytical procedures used for determining the polluttional status of material to be disposed of.

The basic analytical procedure in the ocean-dumping criteria is referred to as the "Standard Elutriate Test" and for it to be applicable and effective, precise implementation guidelines are required. Guidelines mutually agreeable to both EPA and the Corps have been developed and were issued within the Corps to District and Division offices in

the form of Engineer Regulation 1130-2-408, dated 17 January 1974. To achieve wider circulation to interested persons and provide a vehicle for an explanation of the rationale for the use of the elutriate test, this report was conceived and published.

This report was prepared by Drs. J. W. Keeley and R. M. Engler of the ODMR based upon their criteria and guideline developmental efforts achieved with the assistance of the following WES personnel: Mr. M. B. Boyd, MAJ F. H. Griffis, Jr., and Drs. J. Harrison, C. J. Kirby, and R. T. Saucier.

Directors of WES during the development of the test procedure and the preparation and publication of this report were BG E. D. Peixotto, CE, and COL G. H. Hilt, CE. Technical Director was Mr. F. R. Brown.

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SUMMARY

This report presents the rationale and guidelines for implementation of the "Standard Elutriate Test" as authorized in Rules and Regulations, Transportation for Dumping of Material into Ocean Waters, Title 40, Chapter 1, Subchapter H, Part 227.61(c), Federal Register, Volume 38, No. 198, 15 October 1973.

Sediments normally contain constituents that exist in different chemical forms and are found in various concentrations in several locations within the sediment. Criteria to predict the pollution potential of dredged material (sediments) must measure the sediment fraction that has a detrimental effect on water quality and the associated biota. Regulatory criteria should differentiate that fraction of a sediment that does not have an adverse effect on the environment from that fraction that does. The immediate bioavailable fraction of a sediment is dissolved in the sediment interstitial water or in an ionic form that is bound to the ion exchange fraction of the sediment. The elutriate test indicates those constituents in the interstitial water and those ions loosely bound to the ion exchange fraction and, therefore, is a viable criterion for estimating the immediate impact on water quality.

Procedurally, a fixed volume of undisturbed bottom sediment from the dredge site is added to a fixed volume of composite receiving water (proposed disposal site water) at a ratio of 1:4, dredged material:receiving water. The mixture is shaken for a specific time under controlled conditions. The sediment is allowed to settle; the supernatant is decanted, centrifuged, and filtered for clarification. The concentration of specific constituents in the clear supernatant (the standard elutriate) from the dredged material/receiving water mixture is compared with the concentration found in the original filtered receiving water.

DISCUSSION OF REGULATORY CRITERIA FOR OCEAN DISPOSAL OF
DREDGED MATERIALS: ELUTRIATE TEST RATIONALE
AND IMPLEMENTATION GUIDELINES

PART I: DISCUSSION

1971 Regulatory Criteria

1. To assess the effects of dredging and disposal of sediment in open waters and to classify such material as either polluted or unpolluted, in 1971 the Environmental Protection Agency (EPA) issued "Criteria for Determining Acceptability of Dredged Spoil Disposal to the Nation's Waters." The criteria for sediments in fresh and marine waters are summarized below.

<u>Chemical Constituent</u>	<u>Concentration Percent (Dry Wt Basis)</u>
Volatile solids*	6.0
Chemical oxygen demand (COD)	5.0
Total Kjeldahl nitrogen	0.10
Oil-grease	0.15
Mercury	0.0001
Lead	0.005
Zinc	0.005

* TVS % (dry) = $1.32 + 0.98 \text{ (COD \%)}$.

2. Since these criteria were issued, there has been much discussion pertaining to the technical relevancy and adequacy of the required procedures. Many of the disadvantages of these criteria were discussed in the U. S. Army Engineer Waterways Experiment Station (WES) Technical Report H-72-8, "Disposal of Dredge Spoil; Problem Identification and Assessment and Research Program Development,"¹ and can be summarized as follows:

- a. Little or no known correlation exists between the concentration of various chemical constituents within sediments subject to dredging and disposal operations and consequent effects on water quality.

- b. Several of the listed variables, most notably volatile solids and chemical oxygen demand, provide little meaningful information when applied to sediments, especially marine sediments.

Criteria Rationale

Pollution status of dredged material

3. Currently, little definitive information is available on the effects of disposal of dredged material known to contain various "pollutants" on water quality or aquatic organisms. Nevertheless, regulatory agencies, faced with the legislative requirement of establishing dredged material criteria, must strive to establish meaningful criteria based on the best possible knowledge, and avoid the tendency to set forth criteria that precede the current technical state-of-the-art. Furthermore, regulatory criteria should be based on laboratory procedures that can be performed satisfactorily in routine testing laboratories as opposed to complicated procedures that can be conducted only in sophisticated research-level laboratories. Finally, in order to be equitable, the required criteria should not be prohibitively expensive.

4. Most of the difficulty surrounding the establishment of criteria centers on the definition and determination of polluted dredged material; that is, to conform to the definition of "polluted," it is necessary to determine prior to the dredging operations whether or not a particular sediment, if dredged, will cause an adverse environmental effect subsequent to disposal. The confusion arises over the fact that the mere presence of a constituent (toxin, biostimulant, etc.) in the sediment does not indicate or predict the nature and significance of adverse effects following disposal. This is because many chemical constituents found in sediments are "unavailable" and do not react as pollutants. The question toward which criteria should be addressed thus becomes: do the dredging and disposal of sediment known to contain various potential pollutants cause these constituents to be released to the water column (dissolved), or in any other way become more available to the biological food web?

5. In response to the requirements set forth in the Marine Protection, Research, and Sanctuaries Act of 1972 (Public Law 92-432) the following laboratory procedure was developed² by the EPA in conjunction with the Corps of Engineers (CE) to determine the pollution status of dredged material prior to ocean disposal. This procedure was published in the 15 October 1973 Federal Register.³

Dredged material will be considered unpolluted if it produces a standard elutriate in which the concentration of no major constituent is more than 1.5 times the concentration of the same constituent in the water from the proposed disposal site used for the testing. The "standard elutriate" is the supernatant resulting from the vigorous 30-minute shaking of 1 part bottom sediment with 4 parts water from the proposed disposal site followed by 1 hour of letting the mixture settle and appropriate filtration or centrifugation. "Major constituents" are those water quality parameters deemed critical for the proposed dredging and disposal sites taking into account known point or aerial source discharges in the area, and the possible presence in their waste of the materials in Subsections 227.22 and 227.31.

Aquatic ecosystem

6. Before further discussion of the criteria, attention is directed to the schematic of the hydraulic dredging process shown in fig. 1.

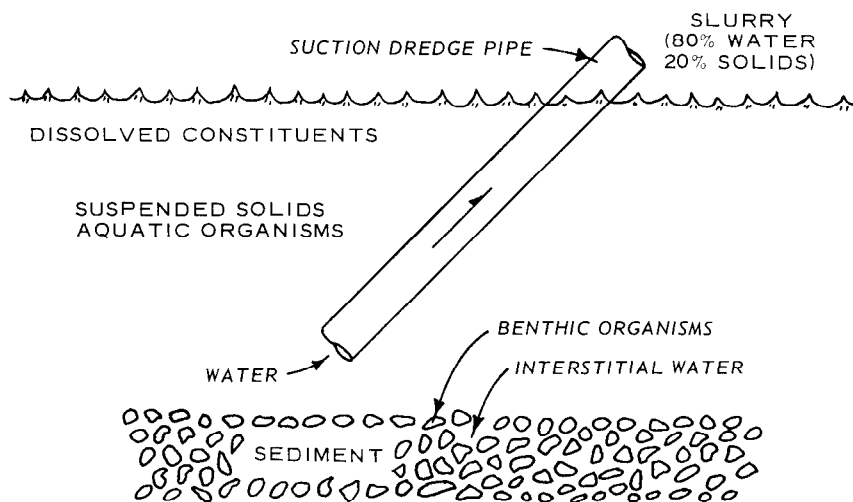


Fig. 1. Hydraulic dredging

This schematic is intended to represent any type of hydraulic dredging whether it be pipeline, hopper, or sidecaster. As shown in fig. 1, hydraulic dredging causes the rapid mixing of two components of the aquatic ecosystem: water and sediment. Sediment is a complex composite of physical, chemical, and biological substances.⁴⁻⁸ Physically,⁹ sediments are comprised primarily of soil materials such as clays, silts, sands, etc., and interstitial water (IW). IW is defined as that water occupying the void between individual sediment particles. Chemically, sediment is known to contain a large and complex variety of constituents that, in one form or another, cover most of the known chemical elements. Bottom sediment is also known to serve as a habitat for a large and complex community of biological organisms collectively known as the benthic community.

7. Bottom sediment chemistry. In order to determine the effect of disposing bottom sediment known to contain various chemical contaminants on water quality and aquatic organisms, at a minimum the chemical form and location of the contaminants within the sediments must be known. A contaminant can exist in many chemical forms in the natural environment and these forms vary from unstable to extremely stable compounds or complexes. The unstable forms are subject to active migration into the biological food web and may range from highly ionized species to soluble, readily available organic complexes. The stable chemical forms may range from highly insoluble inorganic precipitates, complexes, compounds, and minerals to very nonreactive organic complexes. These stable and usually nonreactive forms constitute the major fraction of most sediments and rarely enter into biological cycles.

8. The chemical form of the contaminant can affect both its relative toxicity and its availability to influence biological communities. An example would be to determine whether or not mercury is in the elemental or the methylated form.

9. The location of chemical constituents within the sediments, which is closely related to the chemical form, also determines the availability of these constituents to influence biological communities and thus their ability to react as pollutants. The chemical constituents

and contaminants can be located within the sediment in a variety of positions. The following are some generalized examples⁴⁻¹³ of sediment/chemical constituent locations.

- a. Dissolved or disassociated in the sediment interstitial water. The IW may make up as much as 50 percent of the volume of a sediment and may contain many chemical forms. Some of these are: oxidized and reduced forms of heavy metals and other ionized cations (Ca^{+2} , Mg^{+2} , K^{+} , Na^{+}); nutrients (NO_3^- , NO_2^- , NH_4^+ , NH_3 , PO_4^{+3} , SO_4^{+2}); organic (carbon, nitrogen, phosphorous, sulfur, chelates); various gaseous forms (CH_4 , S^- , H_2S , HS^- , metallic, nitrogenous); inorganic (carbonaceous, siliceous, chlorides, etc.) These forms have the most immediate effect on changes in the water column; however, the IW may contain only 0.1-10 percent of the total chemical constituency of a sediment.
- b. Adsorbed (ionically bound) to charged mineral and organic surfaces (exchangeable). This location is predominated by cations because of the anionic nature of sediment inorganic and organic fractions. These cations consist of the bases, heavy metals and NH_4^+ . Anionic adsorption is negligible because of its pH dependence. The exchangeable fraction is in rapid equilibrium with the IW and acts as a reserve to replace those cations that are removed biologically and chemically from the IW. The chemical forms found in this location may have a longer term effect on water quality by acting as a replacement reserve for constituents that are removed from the IW. This fraction may make up 1.0-20 percent by weight of the total chemical constituency of a sediment.
- c. Oxides, hydroxides, and hydrous oxides of manganese and iron that exist as particulate coatings or discrete particles. This sediment fraction is more commonly known as the reducible (redox) phase which will dissolve under reducing (anaerobic) conditions or form insoluble and stable precipitates under oxidizing (aerobic) conditions. Several toxic heavy metals (Zn, Cu, Cd, Ni, Co, Hg) are known to be physically entrapped in these coatings and particles and may come into solution during anaerobic conditions or may be scavenged from the water phase where an anaerobic sediment is oxidized. As much as 50 percent by weight of the total Fe and Mn is found in this sediment location. Widely varying amounts (even though only trace amounts) of other heavy metals are found here.
- d. Those chemicals that are associated with or are an integral part of the sediment organic fraction. This location contains many chemical compounds and complexes that vary in stability from immediately bioavailable, easily decomposable, moderately decomposable, to resistant to

decomposition. Chemical constituents affiliated with the organic fraction may be incorporated into the food web or migrate to the aqueous phase with potential for long-term effects depending on the nature and degree of microbial degradation. Some heavy metals may be enriched in this phase which is also an important source of phosphorus, ammonium, and sulfur. On the other hand, some products of organic matter decomposition may act as scavengers of some toxic heavy metals. The organic concentration of sediments varies widely but would rarely exceed 10 percent by weight of the total.

- e. The residual phase. This phase is the major location of most chemical species in the sediment and consists of combinations of most primary and secondary weathered minerals occurring in the lithosphere. The locations of many diverse chemical forms are in the inner layer positions of clay minerals or within the mineral crystalline lattice. This phase is very stable and only geologic weathering processes over very long time intervals result in migration of the bound constituents. The residual phase is highly crystalline and as a general example may contain quartz, feldspars, micas, chlorite, kaolinite, illite, montmorillonite, and many different ore forms. This sediment phase contains as much as 75 percent or more by weight of the total concentration of most chemical constituents in a stable, unavailable form. Those constituents dissolved in the water, those that readily dissolve, and those that are ionically exchangeable are generally considered the ones most available to biological communities. The constituents located within the crystalline lattice are considered the ones least available to biological communities.

10. Water column. The water column above the sediment is also a complex system of physical, chemical, and biological processes. As within the sediments, chemical constituents either may be dissolved or affiliated with suspended sediment particles in any of the manners listed above.

11. It is generally assumed that the surface layer of sediment is in dynamic equilibrium with the overlying water. There may be movement of dissolved chemical constituents from the bottom sediments to the overlying water or vice versa. This depends on the dynamic physicochemical state of the sediment and the overlying water at the sediment-water interface.⁶⁻⁹ However, deeper sediment may not be in equilibrium with the overlying water; therefore, in dredging, these deeper sediment

particles are exposed for a short period to the overlying water during hydraulic transport. It is thus reasonable to assume that when these sediments are exposed to the overlying water during dredging, there could be changes in aqueous chemical concentrations.

12. As mentioned earlier, it is generally assumed that chemical constituents in the dissolved state are in a form most available to influence biological communities. One form of dredged material criteria can thus be based on the changes in dissolved chemical concentrations.

Present Criteria

Application

13. The criteria for the ocean dumping of dredged materials described in the Federal Register^{2,3} are based on the amount of change of dissolved chemical concentrations that might be expected to occur due to hydraulic dredging. The standard elutriate test is designed to measure that amount of any chemical constituent that is dissolved in the IW and also measures those constituents that, due to dredging, migrate from the solid phase (sorbed, organic, etc.) to the dissolved phase. The elutriate test procedure is given in Part II.

14. A schematic of the criteria is shown in fig. 2. As shown in the schematic, water and sediments in a ratio approximating a normal hydraulic dredge pumping ratio are placed in a container and vigorously agitated. Also, prior to mixing water with the sediments, dissolved concentrations of the ambient water are determined and listed as X_i . After 30 min of shaking the sediment/water suspension, this mixture is allowed to settle for 1 hr. The supernatant is then filtered and analyzed for the same chemical constituents as determined previously for the ambient water and is labeled X. If the concentration of chemical X (after shaking) is found to be greater than 1.5 times the ambient concentration (X_i), the pollution criterion is exceeded. Thus, if the ambient concentration of lead in the water before shaking is 10 mg/l ($X_i = 10 \text{ mg/l}$), then the dissolved concentration of lead after shaking should not exceed 15 mg/l ($X = 15 \text{ mg/l}$).

CRITERIA FOR OCEAN DISPOSAL OF DREDGED MATERIAL

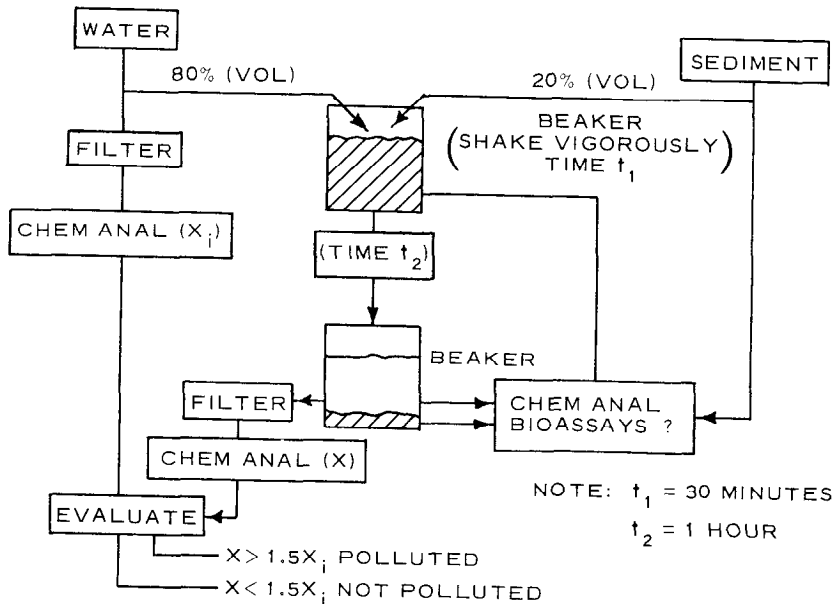


Fig. 2. Elutriate test

Limitations

15. It is stressed that the criteria are considered interim and through intensive research should be continuously improved and updated. Improvement of the criteria not only should include the mechanics of the operation but address interpretation of the analytical results and any additional analyses that may be run on the elutriate. Bioassay¹⁴ should be considered when further research has developed an implementable and reliable procedure for sediments. At this writing, however, bioassay has not been developed to address contaminated dredged material or for the elutriate in either the marine or freshwater environment. Other future research may include use of a weak chemical ion exchange extractant¹⁵ in place of the disposal site water to enable prediction of longer term fate of contaminants.

16. Two important questions have arisen concerning the criteria given in the Federal Register. The first concerns whether or not water from the proposed project site (dredging site) should be mixed with the sediments or whether water from the proposed disposal site should be used. It can be argued that water from the project site should be

used since the test is designed to simulate the hydraulic dredging process. The ratio of sediment to water approximates the normal hydraulic pumping ratio, the vigorous shaking simulates the actual hydraulic dredging process, and during this process net changes in dissolved concentrations may occur. On the other hand, this does not necessarily take into account changes that may occur at the disposal site due to environmental conditions different from the dredging site (different water chemistry).

17. It would be possible to design a test based on the disposal site. In such a procedure, sediments from the project site would be mixed with water from the disposal site in a ratio that approximates an estimated disposal ratio of solids to water. However, if dilution at the disposal site is as great as expected, it is doubtful that changes in dissolved chemical concentrations could be detected in a laboratory test based on this ratio. Results from the procedure set forth in the Federal Register (hydraulic pumping ratio but using water from disposal site) will be largely a function of any differences in water quality between the project site and the disposal site.

18. The second question concerns the 1.5 factor. This number has no toxicological or any other ecological basis. It is meant instead to serve as a guide for the amount of increase in dissolved chemical concentrations that should be allowed before taking into account dilution at the disposal site. However, if dissolved concentrations using project site water do not exceed the 1.5 factor, it is thought that dilution at the disposal site will reduce dissolved concentrations below any harmful levels. This number, and the rest of the procedure, is only an interim guideline that should be improved with further research.

Further development

19. Currently, research is under way by WES personnel and with contract efforts to characterize thoroughly the elutriate test for identification of problems, to develop guidelines for implementation, and for the further development of criteria to determine the pollution capability of dredged material.

PART II: STANDARD ELUTRIATE TEST

1. PROCEDURE

1.1. Collect a water sample at the proposed disposal site and fill a clean polyethylene (glass for special analyses) bottle; seal and immediately store at 4 C. This should be a composite sample, made up of equal volumes of water taken from the upper third, middle third, and bottom third of the water column. Storage in ice at 4 C is recommended to minimize biochemical and chemical changes prior to analysis. Two gallons* of composite receiving water sample would be ample for most analyses; however, more or less sample can be taken as needed. Analysis should be carried out as soon as possible, within 24 hours of sampling if at all possible.

1.2. An appropriate portion of the composite receiving water sample should be filtered through a 0.45-micron membrane filter that has been prerinsed with about 100 ml of the same water. If the receiving water contains a high concentration of suspended solids, centrifugation may be needed prior to filtration. The filtered sample is then analyzed for the concentration of the desired dissolved constituents (X_i). The remainder of the unfiltered sample should be stored in a refrigerator at 4 C until needed for the extraction procedure.

1.3. About a 1-gal sample of bottom sediment to be dredged should be taken with an appropriate grab or core sampler. The sediment (dredged material) should be sealed immediately in plastic jars or bags and stored in ice at 4 C until used in the extraction test. Freezing of the samples should be avoided if at all possible because of anomalous results. It is important that the polyethylene jars be filled to capacity and sealed airtight to minimize any air oxidation that might occur during transportation to the laboratory.

1.4. The dredged material and unfiltered composite disposal site water are mixed in a volumetric 1:4 ratio of dredged material:disposal site water. This is best done by the method of volumetric displacement.

* Multiply gallons by 3.785412 to obtain liters.

One hundred milliliters of unfiltered disposal site water is placed into a 2000-ml graduated wide mouth Erlenmeyer flask. Dredged material is carefully added until the mixture reaches a volume of 300 ml. A 200-ml volume of dredged material will now be in the flask. The flask is filled to 1000 ml with unfiltered composite disposal site water, giving a final volume ratio of 1:4, dredged material:disposal site water.

1.5. The flask is stoppered tightly with a polyethylene stopper or polyethylene-coated rubber stopper, and shaken vigorously on a mechanical shaker for 30 min. After shaking, the suspension is carefully decanted, centrifuged, and filtered through a 0.45-micron membrane filter to give a clear final solution (the standard elutriate). The standard elutriate should be stored in clean polyethylene bottles and aliquots drawn from these bottles for specific analysis (X).

1.6. It is extremely important that all the bottles, flasks, etc., are clean to minimize any trace element contamination. Transportation and storage of dredged material and disposal water at 4 C are very important so as to minimize any biochemical changes that might occur.

2. CALCULATIONS AND EVALUATION

The calculation required is a comparison of

$$X \text{ with } 1.5X_i$$

where X_i = concentration of specific constituent in filtered, composite, receiving site water sample

X = concentration of same constituent in the standard elutriate

$1.5X_i$ = pollution criteria as established by the leaching test

If $X < 1.5X_i$, the constituent does not exceed the pollution criteria.

If $X > 1.5X_i$, the constituent does exceed the pollution criteria.

3. SOME COMMENTS ON EVALUATION

3.1. It shall be borne in mind that ultimately there are at least two reasons for sampling a dredge site; namely, to characterize the

dredge site, and to help assess the environmental impact associated with the release of dredged material into a receiving system.

3.2. With this in mind, it is obvious that the number of samples to be taken at the dredge site needs to be considered rather carefully. Some of the factors which determine the optimum number of samples in a study of this type include:

- a. Cost and availability of adequate sampling and analysis facilities.
- b. Time available for sampling program.
- c. Geographical location of the dredge site.
- d. History of the dredge site.
- e. Area of the dredge site.
- f. Depth of the dredge site.
- g. Homogeneity of the dredged material.
- h. Precision of sampling methods.
- i. Precision of analytical methods.

3.3. The optimum number of replicate analyses of a given sample for each constituent should take into account the expected precision of the analytical method. In no case should less than a duplicate analysis be made for a particular constituent in a given sample.

3.4. Sampling and analysis programs are generally time-consuming and expensive. The results of such programs are major decision factors in dredging operations; therefore, all available information regarding a dredging site and receiving site should be gathered, kept up to date, and used to the fullest possible extent. Insofar as possible, this should be done prior to, or at least in conjunction with, the designing of any sampling program. Wherever possible, individuals familiar with the region, dredge site, and/or disposal site should be located; their advice and information should be considered when designing a sampling program.

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Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U. S. Army Engineer Waterways Experiment Station Vicksburg, Mississippi		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE DISCUSSION OF REGULATORY CRITERIA FOR OCEAN DISPOSAL OF DREDGED MATERIALS: ELUTRIATE TEST RATIONALE AND IMPLEMENTATION GUIDELINES			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final report			
5. AUTHOR(S) (First name, middle initial, last name) John W. Keeley Robert M. Engler			
6. REPORT DATE March 1974		7a. TOTAL NO. OF PAGES 18	7b. NO. OF REFS 15
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) Miscellaneous Paper D-74-14	
b. PROJECT NO.			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Office, Chief of Engineers, U. S. Army Washington, D. C.	
13. ABSTRACT This report presents the rationale and guidelines for implementation of the "Standard Elutriate Test" as authorized in Rules and Regulations, Transportation for Dumping of Material into Ocean Waters, Title 40, Chapter 1, Subchapter H, Part 227.61(c), Federal Register, Volume 38, No. 198, 15 October 1973. Sediments normally contain constituents that exist in different chemical forms and are found in various concentrations in several locations within the sediment. Criteria to predict the pollution potential of dredged material (sediments) must measure the sediment fraction that has a detrimental effect on water quality and the associated biota. Regulatory criteria should differentiate that fraction of a sediment that does not have an adverse effect on the environment from that fraction that does. The immediate bioavailable fraction of a sediment is dissolved in the sediment interstitial water or in an ionic form that is bound to the ion exchange fraction of the sediment. The elutriate test indicates those constituents in the interstitial water and those ions loosely bound to the ion exchange fraction and, therefore, is a viable criterion for estimating the immediate impact on water quality. Procedurally, a fixed volume of undisturbed bottom sediment from the dredge site is added to a fixed volume of composite receiving water (proposed disposal site water) at a ratio of 1:4, dredged material:receiving water. The mixture is shaken for a specific time under controlled conditions. The sediment is allowed to settle; the supernatant is decanted, centrifuged, and filtered for clarification. The concentration of specific constituents in the clear supernatant (the standard elutriate) from the dredged material/receiving water mixture is compared with the concentration found in the original filtered receiving water.			

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Unclassified
Security Classification

14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Dredge spoil						
	Elutriation						
	Environmental effects						
	Laboratory tests						
	Ocean dumping						
	Sediments						
	Water quality control						

In accordance with ER 70-2-3, paragraph 6c(1)(b), dated 15 February 1973, a facsimile catalog card in Library of Congress format is reproduced below.

Keeley, John W

Discussion of regulatory criteria for ocean disposal of dredged materials: elutriate test rationale and implementation guidelines, by J. W. Keeley and R. M. Engler. Vicksburg, U. S. Army Engineer Waterways Experiment Station, 1974.

vii, 13 p. illus. 27 cm. (U. S. Waterways Experiment Station. Miscellaneous paper D-74-14)

At head of title: Dredged Material Research Program.
Sponsored by Office, Chief of Engineers, U. S. Army.
Literature cited: p. 13.

1. Dredge spoil. 2. Elutriation. 3. Environmental effects. 4. Laboratory tests. 5. Ocean dumping. 6. Sediments. 7. Water quality control. I. Engler, Robert M., joint author. II. U. S. Army. Corps of Engineers. (Series: U. S. Waterways Experiment Station, Vicksburg, Miss. Miscellaneous paper D-74-14)
TA7.W34m no.D-74-14